The Effects of Sea Salts on the Forms of Nitrogen Released From Estuarine and Freshwater Sediments: Does Ion Pairing Affect Ammonium Flux?[1]

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ABSTRACT: In sediments with oxidized surface layers, the percentage of mineralized nitrogen that is nitrified/denitrified, compared with that released directly as ammonium, appears to be affected by the presence of sea salts. In estuarine systems, a significant portion of the nitrogen is released as ammonium, whereas in freshwater systems, most of the mineralized nitrogen is often released from the sediments as nitrogen gas. We hypothesized that this discrepancy is caused by differential competition between physical diffusion and nitrification/denitrification in the two systems. The vertical migration (by Fickian diffusion) of ammonium out of the oxic layer may be hindered by cation exchange (or sorption) interactions with sediment particles to a greater extent in fresh water than in estuarine systems. The resulting relatively long residence time, and potentially high levels of particle-bound ammonium in the freshwater sediments, would favor nitrification as the major ammonium removal process. By contrast, ion pair formation of ammonium with seawater anions and blockage of sediment cation exchange sites with seawater cations may allow a sizable fraction of the ammonium to diffuse out of estuarine sediments before it is nitrified. A salt effect, consistent with this hypothesis, has been demonstrated in experimental systems by changing the ionic composition of water flowing above intact cores of freshwater and estuarine sediments. Steady-state ammonium release from Lake Michigan sediments was substantially enhanced in the presence of 30% seawater over that in the presence of lake water alone. Likewise, steady-state ammonium release, from Ochlockonee River and Bay sediments (Florida) and from Toms River and Barnegat Bay sediments (New Jersey), was usually higher in the presence of diluted synthetic seawater than it was in the presence of fresh water.

Introduction

Mechanisms supplying available nitrogen to the euphotic zones of aquatic ecosystems are important, particularly in marine-coastal regions and estuaries, because primary production is often limited by nitrogen supply rates (Ryther and Dunstan

1971). In addition to being supplied from outside sources (tributary and atmospheric inputs, direct discharge from treatment plants, nitrogen fixation), nitrogen is cycled internally in both the water column and sediments (Nixon 1981; Nowicki and Nixon 1985; Pilson 1985). Organic nitrogen is transformed by heterotrophic microorganisms and animals to ammonium that may either be used directly by phytoplankton and other plants or be converted by microbes to nitrates (including ni-
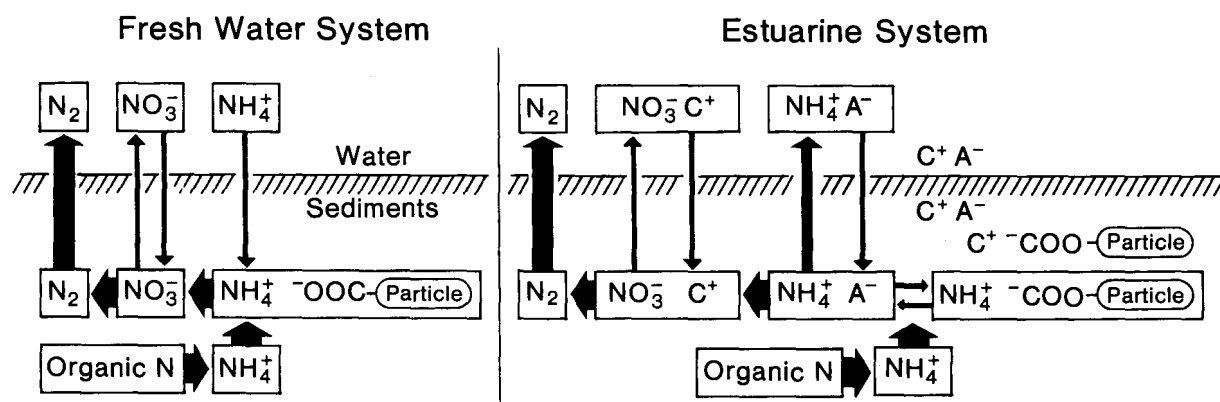
Fresh Water System   Estuarine System

Fig. 1.   Conceptual model of differential ammonium release between freshwater and estuarine (or coastal marine) sediments. Ion pairing is indicated by the coupling of anions (A⁻) and cations (C⁺) in the diagram.

trite) in the presence of oxygen (Henriksen and Kemp 1988; Jenkins and Kemp 1984; Nishio et al. 1983). The nitrates in turn may also be used by plants or may be denitrified (in sediments with anoxic sites) by microorganisms.

Ammonium produced in anoxic sediments equilibrates between the sediments and pore water and is in part diffused to the surface layers of the sediments (Rosenfield 1979). The rate of production of ammonium or other solutes in anoxic sediments can be estimated by kinetic diffusion-reaction models (e.g., Berner 1980). However, if oxygen is present at the sediment surface, such models do not adequately predict actual ammonium flux into overlying waters (e.g., Ulman and Aller 1989), probably because a portion of the ammonium is oxidized to nitrate. The nitrate in turn may be completely or partially denitrified to nitrogen gas in adjacent sites (Jenkins and Kemp 1984; Nishio et al. 1983; Seitzinger et al. 1984). Understanding the mechanisms that control the extent of these different transformations in sediments is necessary because the amount of mineralized nitrogen that is ultimately available to primary producers is decreased by the amount that is denitrified.

Comparison of nitrogen-flux data in estuarine and freshwater environments indicates pronounced differences in the relative amounts of nitrogen forms that are released from oxidized surface sediments (Seitzinger 1988; Seitzinger et al. 1991). In both systems, nitrogen gas and some nitrate are released from sediments with oxic and anoxic sites. Ammonium constitutes a substantial portion of the sediment-water flux of nitrogen in estuaries and coastal marine systems (Blackburn and Henriksen 1983; Nowicki and Nixon 1985), but ammonium often accounts for only a negligible fraction of the nitrogen flux in some freshwater systems with oxic sediment surfaces (Gardner et al.

1987; Seitzinger 1988). Reasons for this difference are not clear. The relatively high levels of sulfate in estuaries cause anaerobic microbial processes (sulfate reduction vs. methanogenesis) to differ between the two salinity regimes (Capone and Kiene 1988), but aerobic microbial reactions are generally functionally similar in marine and freshwater environments (Cole et al. 1988; Hobbie 1988).

We hypothesized that differences in ammonium release between the two systems result from different degrees of ammonium diffusion through the surface layers of the two types of sediments (see conceptual model, Fig. 1). Whereas adsorption or cation exchange sites (e.g., particle associated humic substances) hinder the mobility of ammonium (Rosenfield 1979) in both types of sediments, sea salts in estuarine waters should partially neutralize the polarity of ammonium ion (by ion pair formation) and also cause the cation exchange sites in the sediments to be mostly occupied with seawater cations (Boatman and Murray 1982). Microbially mediated nitrification of the ammonium may keep exchangeable ammonium at low levels in the oxic zone of the freshwater sediments so that any new ammonium produced in, or diffused into, this zone would be attracted to the cation exchange sites rather than be rapidly diffused out of the sediments. Thus, in freshwater sediments, nitrification would be favored by the increased residence time of ammonium in the oxidized layer, whereas in estuarine sediments a portion of the ammonium may diffuse relatively freely out of the sediments before it is nitrified. Assuming, for the sake of simplicity, that the supply rates are the same in both systems, the steady-state concentration of ammonium (not considering denitrification) would also be lower in the estuarine than in the freshwater sediments as a result of diffusive removal. Because nitrification rates are directly dependent on am-

monium concentrations, the presence of sea salts would thus lower the total nitrification rates in the sediments.

If such a hypothesized salt effect scenario is correct, it should be possible to modify ammonium release patterns in freshwater and saltwater sediments, respectively, by changing the salinity of the interstitial and overlying waters. We tested this hypothesis by comparing fluxes of ammonium and nitrate from freshwater and estuarine sediments into oxygenated fresh and salt water that was passed slowly over intact cores.

Methods

SEDIMENT SAMPLES

Lake Michigan is a temperate, mesotrophic Laurentian Great Lake in the northern United States where denitrification and sediment-water nitrogen fluxes have previously been measured at two stations (Gardner et al. 1987). Two cores of silty Lake Michigan sediments were taken from a relatively intact grab sample that had been collected at a 45-m deep station offshore from Grand Haven, Michigan, in April 1988 and stored in the laboratory at 4°C for 2 d until the experiment was begun.

The Ochlockonee River, Florida, is the major freshwater input to the Ochlockonee Bay and drains the St. Mark's National Forest and Wildlife Refuge. It is a relatively unpolluted blackwater river; there are no known sewage plants or industrial discharges along the length of the river (Seitzinger 1987). The bay sediments consisted of soft mud and were collected at an upper bay location, used previously for studies of sediment-water nutrient fluxes and denitrification studies (Seitzinger 1987). Salinity at the time of sediment collection was 12‰. Ochlockonee River sediments were collected approximately 12 km upstream from the head of the bay, above any saltwater intrusion. The river sediments were soft silt mixed with some fine sand and decomposing leaves and detritus from the trees and vegetation lining the shore. Both river and bay samples were collected as intact cores by divers in May 1988 and shipped to the laboratory as intact subcores in the experimental chambers (see below). The cores were held at room temperature during shipping and storage until experiments were started 5 days after collection.

Barnegat Bay is a shallow estuary located behind a series of barrier islands in New Jersey. Sediments collected from the bay were dark brown silt-clay sediments. The bottom waters are well oxygenated and the salinity at the collection site was 22‰. Toms River is the major freshwater riverine input to Barnegat Bay. Toms River sediments were collected

upstream from the drinking water intake for the town of Toms River. The sediments were silty-sand and contained some visible pieces of decomposing leaf litter. Toms River and Barnegat Bay cores were sampled by divers in July 1988 and transferred intact at room temperature to the laboratory in Ann Arbor, Michigan, where experiments were done. Water above the cores was areated with a battery-driven aquarium pump during transport. Subcores were placed in the experimental chambers and the experiment was begun three days after sample collection.

EXPERIMENTAL APPARATUS AND PROCEDURES

A continuous flowcell system with intact cores was designed to examine directly the effects of sea salts on ammonium release from sediments to overlying waters (Fig. 2). Each flowcell was constructed from a 60-ml plastic syringe (2.5 cm I.D.). A plastic frit (from a Waters Sep Pac column), mounted in a cored rubber plunger tip, was placed at the bottom of the flowcells used for Lake Michigan and Ochlockonee cores to allow the pore water to be purged upward through some of the cores. The frit was not used in the Toms River/Barnegat Bay study since the pore waters of these cores were not purged at the beginning of the experiment. A second inlet tube and an outlet tube were mounted in the plunger of the syringe (Fig. 2) so that water of the desired salinity could be passed over the surface of the cores.

Intact cores with overlying water were obtained, using a truncated 60-ml plastic syringe, and carefully transferred, by pushing down with the sampling-syringe plunger, directly into the experimental flowcell assembly. A rubber seal arrangement (constructed from a folded section of bicycle inner tube) (Fig. 2) was used to connect the coring tube to the flowcell barrel during the transfer. The influence of the ionic composition of water on the transfer of ammonium from estuarine and freshwater sediments, respectively, was examined by exposing sequentially both types of sediments to slow (4 ml h^{-1}) flows of salt water and fresh water. The water had the exact or approximate ionic composition of either lake water (Lake Michigan water or low-nutrient culture water, Lehman 1980) or estuarine water (either seawater diluted with lake water or diluted synthetic ocean water (DSOW) was equal to artificial seawater (Parsons et al. 1984) diluted with low-nutrient culture water). The artificial preparations were fortified with approximately natural levels of ammonium and nitrate (see figure legends for exact concentrations). The concentrations of ammonium in the inflowing waters (0.5 μM to 2 μM) were low compared to concen-
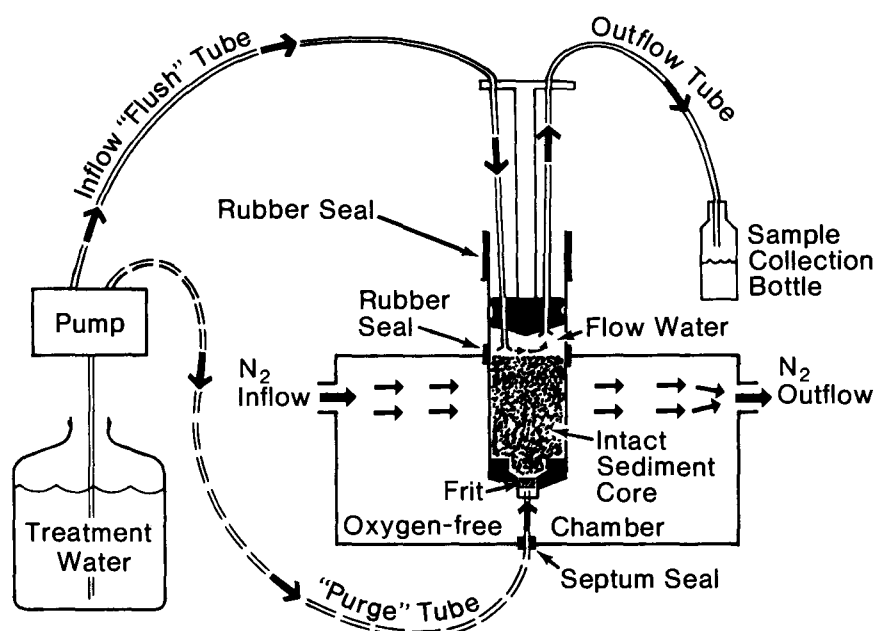
Fig. 2. Schematic diagram of flowcell system used to measure fluxes of ammonium and nitrate from intact sediment cores into the overlying water. Freshwater or diluted synthetic ocean water (DSOW) was pumped (at a rate of 4 ml h^{-1}) through the inflow tubes except when cores were purged for 2 d at the beginning of the experiment. For purging, the normal inflow tube was plugged and the inflow water was passed upward through the core, as indicated by the dashed-line tube. The nitrogen gas maintained an oxygen-free environment around the portions of the cores that would normally be anoxic. It was used in both of the estuary/river comparisons but not for the preliminary experiment on Lake Michigan sediments.

trations expected for subsurface sediment pore waters (Fitzgerald 1989) and should not have substantially affected the direction of the ammonium flux. They did, however, place an upper limit on the extent of negative flux that could be observed during an experiment. Oxygen-free artificial freshwater or diluted saltwater was pumped slowly (2–4 ml h^{-1}) through the sediments of some of the cores (with a Manostat Cassette Pump, Standard Model) to purge the original pore water and replace it with water of the desired ionic composition. (Note in this paper, purging refers to the passage of water through the sediment cores, whereas flushing refers to the passage of water over the sediment surfaces.)

In the preliminary experiment on Lake Michigan sediments, ammonium release-uptake from a sediment core flushed with diluted sea water (3 volumes seawater: 7 volumes lake water) was compared to that for a core flushed with lake water. The experimental systems were held at 4°C, the approximate in situ temperature. The samples were purged overnight with the respective experimental waters and then flushed at flow rates of ca 4 ml h^{-1}.

For the estuarine comparisons, a multiunit system was constructed to handle up to 14 cores and maintain an oxygen-free environment around the

anoxic portions of the cores, as shown in Fig. 2. The multiunit system allowed us to examine simultaneously the ammonium flux from both river and estuarine sediment cores flushed with freshwater and simulated estuarine water, respectively. The anoxic portions of the flowcells were sealed into a gas-tight chamber that was continuously flushed with nitrogen gas to prevent oxygen from diffusing through the plastic cylinder walls of the syringe barrel (Fig. 2).

Experiments were conducted at room temperature. Some of the cores in the Ochlockonee comparison were initially purged to displace the pore water with water of the desired salt content. The approximate purging volume required to displace the salt in the pore and overlying water was determined by monitoring the outflowing water daily with a refractometer. For the remainder of the cores, water was continuously flushed over the top surfaces of the sediments at a rate of ca 4 ml h^{-1}. After 2 days, when the salinities of water passing through the estuarine sediments purged with NOPN reached ca zero ‰, flow of deoxygenated water through the sediments was discontinued and oxygenated water was then flushed over the surfaces of all the sediment cores.

The fluxes of ammonium and nitrate from (or into) the sediments was determined by multiplying

the changes in ammonium and nitrate concentrations between the inflowing and outflowing waters times the measured flow rates of the water passing over the cores. Ammonium was measured by liquid chromatography (modification of Gardner 1978) and nitrate by auto analyzer with discrete injection (Gardner and Malczyk 1983). Measurements were usually made daily.

The ionic composition of the flushing waters was switched for all of the treatments after the nitrogen fluxes for the various treatments reached apparent steady-state (10 or 11 d). The ammonium and nitrate fluxes were then followed for an additional 7 to 9 d.

Results

LAKE MICHIGAN

The Lake Michigan core that was purged and flushed with diluted seawater consistently released more ammonium than the parallel core exposed to lake water (Fig. 3). Ammonium flux from the diluted sea water treatment ranged from about 30 μmol NH_4^+ m^{-2} h^{-1} during the initial flushing period to a steady-state release rate of about 4 μmol NH_4^+ m^{-2} h^{-1}. The initial elevated, but decreasing, levels of ammonium can be attributed to the displacement of exchangeable ammonium in the sediments by the seawater salts, whereas the steady-state flux of ammonium after day 4 can be attributed to ammonium production in the sediments due to organic nitrogen mineralization. In contrast, the sediments flushed with lake water released only about 3 μmol NH_4^+ m^{-2} h^{-1} the first day and actually removed ammonium from the overlying waters under steady-state conditions later in the experiment (Fig. 3). The net steady-state difference in ammonium flux between the two cores was about 8 μmol NH_4^+ m^{-2} h^{-1}.

OCHLOCKONEE RIVER—OCHLOCKONEE BAY COMPARISON

Ammonium flux into the overflowing water of previously-purged cores reached steady-state within a day after the two-day purge for both freshwater- and DSOW-treated cores (Fig. 4) but did not reach steady-state in the nonpurged cores until after 4 to 8 d of flushing (Fig. 5).

Ammonium was not released from any of the Ochlockonee sediments that were flushed first with fresh water except for the first few measurements on the nonpurged bay sediments (Fig. 5) when salts were apparently still present in the surface sediments. After an initial equilibration period of about 5 d, the direction of ammonium flux was from the water to the sediments (i.e., a negative flux from the sediments) in all the freshwater-flushed cores
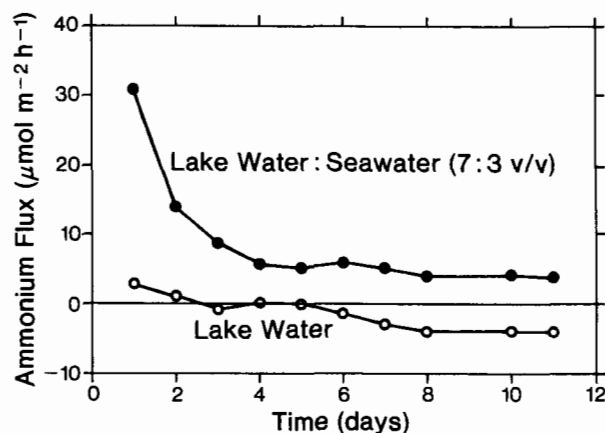
Fig. 3. Ammonium flux from Lake Michigan sediments under flowing lake water and a lake water : sea water mixture, 7: 3 by volume. Ammonium concentrations in the inflowing lake water and in the mixture were 0.7 and 0.5 μM, respectively.

(Figs. 4 and 5). However, in the presence of DSOW, ammonium was released from all the river sediments and from the unpurged bay sediments. The purged bay sediments showed a moderate uptake of ammonium from the water (Fig. 4).

After 10 days of incubation, when the ammonium fluxes appeared to have reached steady-state, ammonium flux in the DSOW-flushed cores ranged from −2 to 44 μmole NH_4^+ m^{-2} h^{-1} [mean ($\pm$ SE) = 14 ($\pm$ 7) μmole NH_4^+ m^{-2} h^{-1}] as compared to a range of −6 to −14 μmole NH_4^+ m^{-2} h^{-1} [mean ($\pm$ SE) = −11 ($\pm$ 1) μmole NH_4^+ m^{-2} h^{-1}] for the freshwater-flushed cores (Figs. 4 and 5). The rates for the DSOW-flushed cores agreed well with previous measurements of ammonium flux measured in 20 cores collected from Ochlockonee Bay at a variety of locations and sampling times [range = −66 to 105 μmole NH_4^+ m^{-2} h^{-1}; mean ($\pm$ SE) = 19 ($\pm$ 9) μmole NH_4^+ m^{-2} h^{-1}] (Seitzinger 1987). Data were not available from Ochlockonee River sediments for comparison with our data for the freshwater-flushed cores, but the observed negative fluxes agree with previous data from other sites (Gardner et al. 1987; Seitzinger 1988) indicating that freshwater sediments with oxic surfaces often do not release a large portion of mineralized ammonium into overlying waters.

Ammonium release rates were reduced in the sediments where the water was switched from salt water to fresh water but increased in the cores where the sequence was reversed. The ammonium flux from the sediments to the water rapidly moved in a positive direction when fresh water overflowing the river sediments was replaced with DSOW (Figs. 4 and 5). The river sediments showed a net release of ammonium in the presence of DSOW for the duration of the experiment, but the two
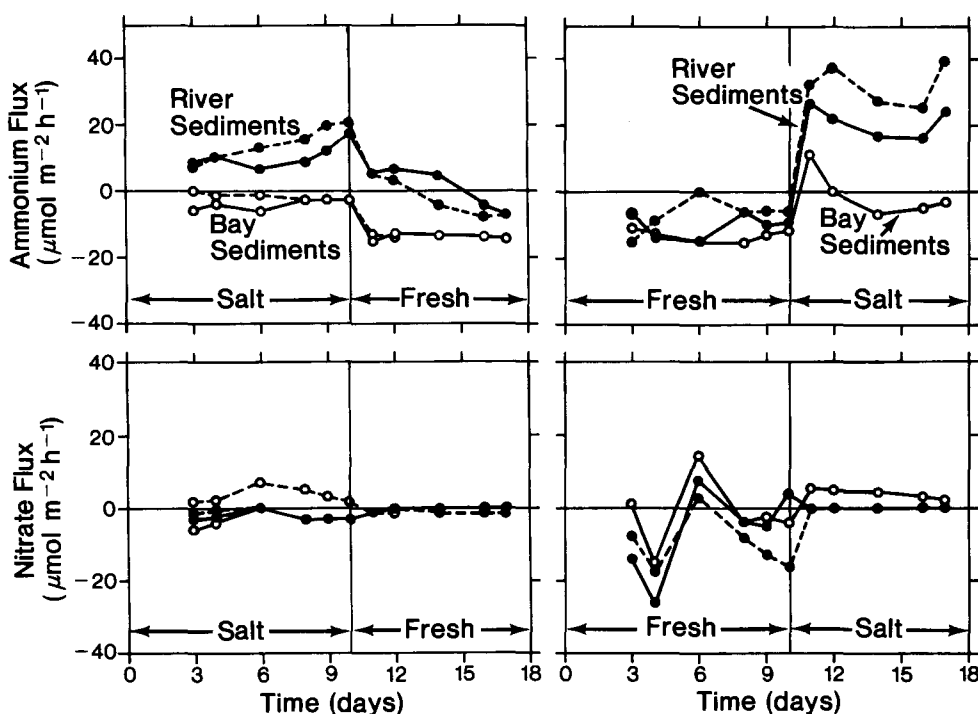
Fig. 4. Ammonium and nitrate fluxes from Ochlockonee Bay and River sediments purged for two days and then flushed with salt water (DSOW) and fresh water, respectively. Ten days after the experiment began, the water composition was reversed for all the cores. Inflowing DSOW contained 9‰ salinity, 1 μM NH_4^+, and 1 μM NO_3^-. Inflowing freshwater contained 2 μM NH_4^+ and 7 μM NO_3^-. RS = river sediments; BS = bay sediments.

bay cores showed slightly negative ammonium fluxes at the end of the experiment.

At the end of the experiment on day 17, ammonium fluxes in the cores that had been switched from freshwater- to DSOW-flushing ranged from -2 to 41 μmole NH_4^+ m^{-2} h^{-1} [mean ($\pm$ SE) = 20 ($\pm$ 10) μmole NH_4^+ m^{-2} h^{-1}]. These rates were not significantly different from rates observed for the DSOW-flushed cores before the switch or from rates previously observed in the bay (see above). On the other hand, ammonium fluxes for the cores that were switched to freshwater ranged from -15 to $+15$ μmole NH_4^+ m^{-2} h^{-1} [mean ($\pm$ SE) = -7 ($\pm$ 5) μmole NH_4^+ M^{-2} h^{-1}] and were not significantly different from the freshwater fluxes before the switch. All fluxes were negative in freshwater-flushed cores except for the river core that had not been purged at the beginning of the experiment; this core showed a positive flux of 15 μmole NH_4^+ m^{-2} h^{-1} at the end of the experiment (Fig. 5).

In contrast to the steady-state patterns for ammonium flux observed after a few days of equilibration, net nitrate flux was more variable with time of incubation during the first half of the experiment; it peaked between 3 and 6 days and then decreased again (Figs. 4 and 5). Fluxes were more variable with time in freshwater than in DSOW treatments. Net nitrate flux was small for all cores during the second half of the experiment (Figs. 4 and 5), probably because any nitrate that was produced was quantitatively denitrified (Gardner et al. 1987).

TOMS RIVER—BARNEGAT BAY COMPARISON

Ammonium release from Toms River sediments differed from that observed in the other freshwater sediments in that significant concentrations of ammonium were released from the sediments in the presence of fresh water as well as in the presence of DSOW (Fig. 6). After about 8 d, under apparent steady-state conditions, more ammonium was released from both the river and estuary sediments into flushing DSOW than was released from similar sediments into fresh water. These latter results agreed with our conceptual model and with the data from Lake Michigan and Ochlockonee sediments (Figs. 3, 4 and 5). However, the results for the second half of the experiment, after the composition of the overflowing waters were switched, did not completely follow our conceptual model predictions. In agreement with the model, ammonium release from the bay sediments decreased when the water was switched from DSOW to fresh
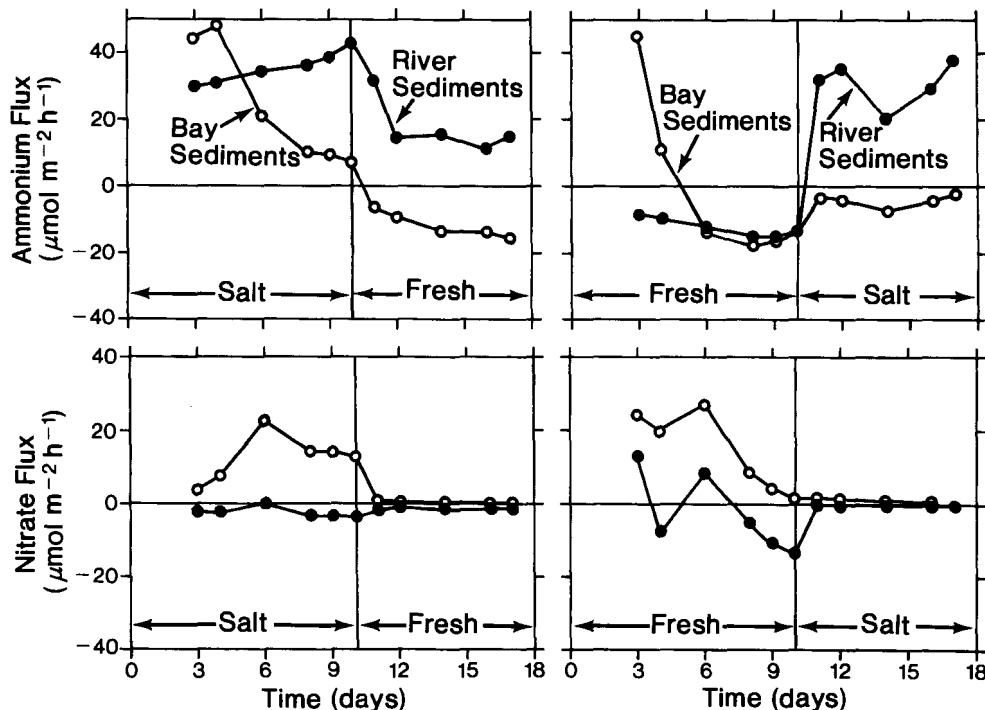
Fig. 5. Ammonium and nitrate fluxes from Ochlockonee Bay and River sediments flushed with salt water (DSOW) and fresh water, respectively. All conditions were the same as for the cores indicated in Fig. 4 except that the cores were flushed rather than purged during the first two days.

water, and release from the river sediments increased when the waters were switched from fresh water to DSOW (Fig. 6). However, in contrast to the predictions of the model, ammonium release from the river sediments did not significantly decrease when DSOW was switched to fresh water nor did the release from the bay sediments increase when fresh water was replaced with seawater (Fig. 6).

Nitrate flux was not measurable from the Toms River sediments in the presence of either fresh water or DSOW (Fig. 6). This result implies either that little or no nitrate was formed in these experimental systems or that all of the new nitrate was quantitatively denitrified. In the bay sediments, some net nitrate release was observed during the course of the incubations but release rates were low regardless of salinity.

Discussion

Our experimental flowcell design allowed direct observation of the effects of increased or decreased salinity on ammonium release from intact sediments. Use of a flow-through rather than a static system for the overlying water prevented the solutes from reaching abnormally high levels in the water and allowed steady-state conditions to develop. A potential problem with suddenly changing

the salinity or oxygen content of the flushing water is that the biota associated with the sediments were undoubtedly affected. Such biological effects are difficult to evaluate, but it was apparent that changing the salt content of the flushing water did not completely kill or inactivate the ammonium producers since ammonium production continued in freshwater sediments that had been treated with saline water. Previous studies, summarized by Henriksen and Kemp (1988), indicate that nitrifying bacteria can acclimate to a broad range of salinities after a lag phase of several days. The biota in the experimental cores were also undoubtedly affected during the 2 to 5 day periods between sampling and the beginning of experiments, but these changes should not invalidate our comparisons because the experimental design balanced freshwater and saltwater treatments for each type of sediment core.

The gradual decrease in ammonium release rates, in the nonpurged bay sediments that were flushed with fresh water (Figs. 5 and 6), suggests that the salt in the layer directly affecting ammonium release was effectively diffused out of the surface sediments into the flushing fresh water during the course of several days. Thus prepurging the cores was not necessary to determine the relative effects of salt water vs. fresh water on ammonium flux if
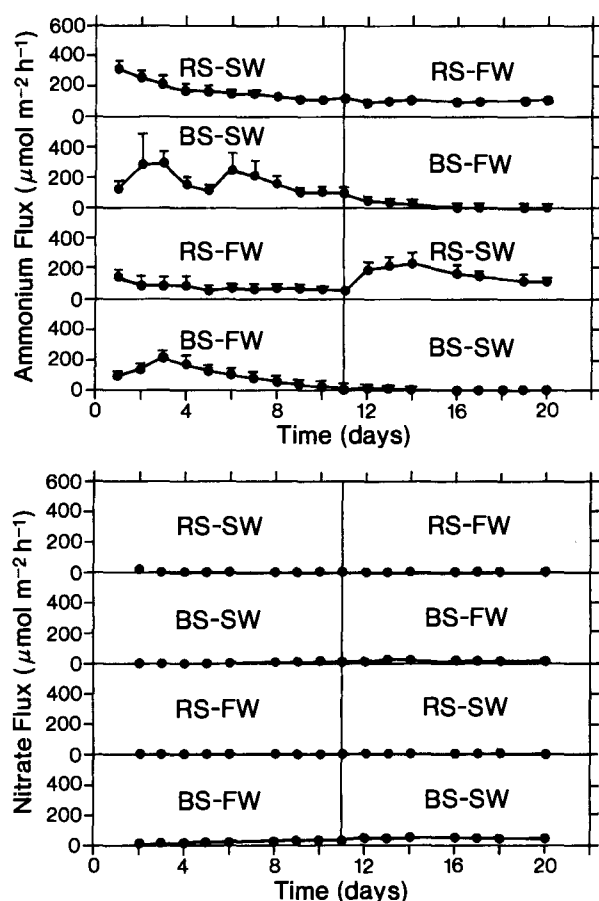
Fig. 6. Ammonium and nitrate fluxes from Barnegat Bay and Toms River sediments flushed with saltwater (DSOW) and freshwater respectively. Eleven days after the experiment began, the water composition was reversed for all the cores. The salinity of the inflowing DSOW was 21‰. The inflowing waters both contained 2 μM NH_4^+ and 1 μM NO_3^-. RS = river sediments; BS = bay sediments; FW = freshwater flush; SW = saltwater flush.

sufficient time was allowed for the cores to equilibrate with the flushing water. Nonpurged cores should have reflected natural conditions better than the purged cores because the original nutrient profiles should have been comparatively undisturbed in the nonpurged cores.

Despite some discrepancies, the flowcell nutrient fluxes reported here, combined with previous flux data mentioned above, are generally consistent with the conceptual model proposed in Fig. 1. With sea salts in the overflowing water, ammonium was often released from the sediments. When ammonium release occurred, the rates of physical diffusion of ammonium out of the sediments was apparently competitive with microbial nitrification as an ammonium removal process. These observations agree with previous data on ammonium release from es-

tuarine sediments (Seitzinger 1988; Seitzinger et al. 1991) and are consistent with the idea that observed differences in sediment-water ammonium release between freshwater and estuarine systems may be directly due to a salt effect. Exceptions to this trend, that could indicate potential deficiencies in our conceptual model, were results from some of the Ochlockonee Bay (Figs. 4 and 5) and Barnegat Bay sediments after fresh water was switched to DSOW (Fig. 6). Exact reasons for these discrepancies are unclear, but they were likely caused by the shifting of microbial assemblages during our experimental manipulations. For example, in the Barnegat Bay cores, where expected ammonium production did not increase after the switch to DSOW, net nitrate release increased slightly throughout the course of the incubation in the presence of both freshwater and DSOW; thus, nitrification may have kept pace with the release of ammonium during our experimental manipulations. In other laboratory experiments, we have observed apparent rapid nitrification-denitrification of ammonium in formerly anoxic sediments during 24-h extractions of exchangeable ammonium with 2 N KCl, when the sediments were not first treated, by heating, to kill nitrifiers (unpublished results).

In the absence of significant concentrations of sea salts, ammonium was usually either not released or was released at lower rates than occurred in the presence of DSOW under steady-state conditions. This result agrees with previous data for lakes and other freshwater systems (Gardner et al. 1987; Seitzinger 1988) and fits our hypothetical model (Fig. 1). Under freshwater conditions, sediment-ammonium binding, presumably by ion exchange or sorption, apparently prevents the free diffusion of ammonium out of oxic sediments and allows quantitative nitrification to occur in the near-surface sediments with oxic sites. Although nitrification of ammonium in the oxidized surface layer is apparently complete, this process is often not fully reflected in measurements of net nitrate fluxes (e.g., Figs. 4, 5 and 6) because often most nitrate produced in sediments is denitrified (Gardner et al. 1987; Seitzinger 1987; Jenkins and Kemp 1984).

In the case of Toms River sediments, ammonium was released under both freshwater and saltwater conditions. This result may reflect the comparatively high nutrient status of the Toms River site, as reflected by the relatively high ammonium release rates in the presence of DSOW at this site (Fig. 6) as compared to the other freshwater sites (Figs. 3, 4 and 5). In a nutrient-rich system, the oxic layer may be relatively thin, and organic nitrogen degradation rates comparatively high. Under these conditions, ammonium ions could poten-

tially be supplied at rates in excess of the nitrifier demand with the result that cation exchange sites in the thin oxic layer could become relatively saturated with ammonium (i.e., in equilibrium with the pore water) even in the absence of sea salts and therefore allow some ammonium to escape. Ammonium release from freshwater sediments has also been observed in other nutrient-rich systems (e.g., Lake Michigan's Green Bay; personal communication, Sharon Fitzgerald, NOAA Great Lakes Environmental Research Laboratory).

The effects of the presence of sea salts on ammonium release from the sediments that were often observed (Figs. 3, 4, 5 and 6) are consistent with the idea that ion pairing is a mechanism that allows a portion of mineralized ammonium to selectively diffuse from estuarine sediments. Ion pairing is a well-known phenomenon that affects the chemistry of various anions and cations in seawater (Riley and Skirrow 1965) and is often used to decrease or increase solute-column interactions in liquid chromatography (e.g., Synder and Kirkland 1979; Mantoura and Llewellyn 1983). However, to our knowledge, ion pairing has not been addressed as an important issue in aquatic nitrogen dynamics. This lack of attention may be in part because available nitrogen usually occurs at low concentrations in marine waters and its concentrations and dynamics are thought to be largely controlled by biological processes. We suggest that ion pairing of ammonium, in conjunction with cation exchange site blockage by seawater cations, may be an important factor affecting the flux of ammonium from estuarine sediments into overlying waters.

ACKNOWLEDGMENTS

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